

10/579971

FP1024

AP20 Rec'd PCT/PTO 23 MAY 2006

HIGH STRENGTH AND HIGH TOUGHNESS MAGNESIUM ALLOY AND
METHOD OF PRODUCING THE SAME

Field of the Invention

5 The present invention relates to a high strength and high toughness magnesium alloy and a method of producing the same, more particularly, a high strength and high toughness magnesium alloy, in which the high strength and high toughness property can be achieved by
10 containing a specific rare-earth element at a specific rate, and a method of producing the same.

Background of the Invention

A magnesium alloy has come quickly into wide use as
15 materials of a housing of a mobile-phone and a laptop computer or an automotive member because of its recyclability.

For these usages, the magnesium alloy is required to have a high strength and high toughness property.
20 Thus, a producing method of a high strength and high toughness magnesium alloy has been studied in many ways from a material aspect and a manufacture aspect.

In a manufacture aspect, as a result of promoting nanocrystallizing, a rapid-solidified powder metallurgy
25 method (a RS-P/M method) has been developed to obtain a magnesium alloy having a strength of about 400MPa as much as about two times that of a casting material.

As a magnesium alloy, a Mg-Al based, a Mg-Al-Zn based, a Mg-Th-Zn based, a Mg-Th-Zn-Zr based, a Mg-Zn-Zr based, a Mg-Zn-Zr-RE (rare-earth element) based alloys are widely known. When a magnesium alloy having the 5 aforesaid composition is produced by a casting method, a sufficient strength cannot be obtained. On the other hand, when a magnesium alloy having the aforesaid composition is produced by the RS-P/M method, a strength higher than that by the casting method can be obtained; 10 however, the strength is still insufficient. Alternatively, the strength is sufficient while a toughness (a ductility) is insufficient. So, it is troublesome to use a magnesium alloy produced by the RS-P/M method for applications requiring a high strength 15 and high toughness.

For a high strength and high toughness magnesium alloy, Mg-Zn-RE (rare-earth element) based alloys have been proposed (for instance, referring to Patent Literatures 1, 2 and 3).

20 Patent Literature 1: Patent Number 3238516 (Fig.1),
Patent Literature 2: Patent Number 2807374,
Patent Literature 3: Japanese patent Application Laid

Disclosure of Invention

25 Problems to be resolved by the Invention

However, in a conventionally Mg-Zn-RE based material, a high strength magnesium alloy is obtained

by, for instance, heat-treating an amorphous alloy material for forming a fine-grained structure. In this case, depending on a preconceived idea in which adding a substantial amount of zinc and rare-earth element is a 5 requirement for obtaining the amorphous alloy material, a magnesium alloy containing relatively a large amount of zinc and rare-earth element has been used.

The Patent Literatures 1 and 2 disclose that a high strength and high toughness alloy can be obtained. 10 However, practically, there are no alloys having enough strength and toughness for putting in practical use. And, currently, applications of a magnesium alloy have expanded, so an alloy having a conventionally strength and toughness is insufficient for such applications. 15 Therefore, a higher strength and higher toughness magnesium alloy has been required.

The present invention has been conceived in view of the above problems. An object of the present invention is to provide a high strength and high toughness 20 magnesium alloy having a strength and a toughness both being on a sufficient level for the alloy to be practically used for expanded applications of a magnesium alloy and a method of producing the same.

25 Means of Solving the Problems

In order to solve the above-mentioned problems, a high strength and high toughness magnesium alloy

according to the present invention contains "a" atomic% of Zn, "b" atomic%, in a total amount, of at least one element selected from the group consisting of Dy, Ho and Er and a residue of Mg, wherein "a" and "b" satisfy the following expressions (1) to (3):

- (1) $0.2 \leq a \leq 5.0$;
- (2) $0.2 \leq b \leq 5.0$; and
- (3) $0.5a - 0.5 \leq b$.

And, each of Dy, Ho and Er are rare-earth element for forming a crystal structure of a long period stacking ordered structure phase in a magnesium alloy casting product.

A high strength and high toughness magnesium alloy according to the present invention contains "a" atomic% of Zn, "b" atomic%, in a total amount, of at least one element selected from the group consisting of Dy, Ho and Er and a residue of Mg, wherein "a" and "b" satisfy the following expressions (1) to (3):

- (1) $0.2 \leq a \leq 3.0$;
- (2) $0.2 \leq b \leq 5.0$; and
- (3) $2a - 3 \leq b$.

And, the high strength and high toughness magnesium alloy preferably comprises a magnesium alloy casting product to which a plastic working is subjected.

A high strength and high toughness magnesium alloy according to the present invention preferably comprises a plastically worked product which is produced by

preparing a magnesium alloy casting product containing "a" atomic% of Zn, "b" atomic%, in a total amount, of at least one element selected from the group consisting of Dy, Ho and Er and a residue of Mg, wherein "a" and "b" 5 satisfy the following expressions (1) to (3), and subjecting said magnesium alloy casting product to a plastic working, wherein said plastically worked product has a hcp structured magnesium phase and a long period stacking ordered structure phase at room temperature:

10 (1) $0.2 \leq a \leq 5.0$;
(2) $0.2 \leq b \leq 5.0$; and
(3) $0.5a - 0.5 \leq b$.

A high strength and high toughness magnesium alloy according to the present invention preferably comprises 15 a plastically worked product which is produced by preparing a magnesium alloy casting product containing "a" atomic% of Zn, "b" atomic%, in a total amount, of at least one element selected from the group consisting of Dy, Ho and Er and a residue of Mg, wherein "a" and "b" 20 satisfy the following expressions (1) to (3), and subjecting said magnesium alloy casting product to a plastic working, wherein said plastically worked product has a hcp structured magnesium phase and a long period stacking ordered structure phase at room temperature:

25 (1) $0.2 \leq a \leq 3.0$;
(2) $0.2 \leq b \leq 5.0$; and
(3) $2a - 3 \leq b$.

A high strength and high toughness magnesium alloy according to the present invention preferably comprises a plastically worked product which is produced by preparing a magnesium alloy casting product containing 5 "a" atomic% of Zn, "b" atomic%, in a total amount, of at least one element selected from the group consisting of Dy, Ho and Er and a residue of Mg, wherein "a" and "b" satisfy the following expressions (1) to (3), and subjecting said magnesium alloy casting product to a 10 plastic working and a heat treatment, wherein said plastically worked product has a hcp structured magnesium phase and a long period stacking ordered structure phase at room temperature:

(1) $0.2 \leq a \leq 5.0$;
15 (2) $0.2 \leq b \leq 5.0$; and
(3) $0.5a - 0.5 \leq b$.

A high strength and high toughness magnesium alloy according to the present invention preferably comprises a plastically worked product which is produced by 20 preparing a magnesium alloy casting product containing "a" atomic% of Zn, "b" atomic%, in a total amount, of at least one element selected from the group consisting of Dy, Ho and Er and a residue of Mg, wherein "a" and "b" satisfy the following expressions (1) to (3), and subjecting said magnesium alloy casting product to a 25 plastic working and a heat treatment, wherein said plastically worked product has a hcp structured

magnesium phase and a long period stacking ordered structure phase at room temperature:

- (1) $0.2 \leq a \leq 3.0$;
- (2) $0.2 \leq b \leq 5.0$; and
- 5 (3) $2a - 3 \leq b$.

And, the long period stacking ordered structure phase preferably has an average particle diameter of $0.2 \mu\text{m}$ or more. The long period stacking ordered structure phase has a number of random grain boundaries 10 contained in crystal grain thereof. And, the crystal grain defined by the random grain boundary preferably has an average particle diameter of $0.05 \mu\text{m}$ or more.

And, in the high strength and high toughness magnesium alloy according to the present invention, the 15 long period stacking ordered structure phase preferably has at least single-digit smaller dislocation density than said hcp structured magnesium phase.

And, in the high strength and high toughness magnesium alloy according to the present invention, the 20 long period stacking ordered structure phase preferably has a crystal grain having a volume fraction of 5% or more.

And, in the high strength and high toughness magnesium alloy according to the present invention, the 25 plastically worked product preferably has at least one kind of precipitation selected from the group consisting of a compound of Mg and rare-earth element, a compound

of Mg and Zn, a compound of Zn and rare-earth element and a compound of Mg, Zn and rare-earth element.

And, in the high strength and high toughness magnesium alloy according to the present invention, said 5 at least one kind of precipitation preferably has a total volume fraction of larger than 0 to 40% or less.

And, in the high strength and high toughness magnesium alloy according to the present invention, the plastic working is preferably carried out by at least 10 one process in a rolling, an extrusion, an ECAE working, a drawing, a forging, a press, a form rolling, a bending, a FSW working and a cyclic working of theses workings.

And, in the high strength and high toughness 15 magnesium alloy according to the present invention, a total strain amount when said plastic working is preferably carried out is 15 or less.

And, in the high strength and high toughness magnesium alloy according to the present invention, a 20 total strain amount when the plastic working is preferably carried out is 10 or less.

In the high strength and high toughness magnesium alloy according to the present invention, Mg preferably contains y atomic% of at a total amount of Y and/or Gd, 25 wherein "y" satisfies the following expressions (4) and (5),

(4) $0 \leq y \leq 4.8$ and

(5) $0.2 \leq b+y \leq 5.0$.

In the high strength and high toughness magnesium alloy according to the present invention, Mg preferably contains "c" atomic%, in a total amount, of at least one 5 element selected from the group consisting of Yb, Tb, Sm and Nd, wherein "c" satisfies the following expressions

(4) and (5):

(4) $0 \leq c \leq 3.0$; and,

(5) $0.2 \leq b+c \leq 6.0$.

10 In the high strength and high toughness magnesium alloy according to the present invention, Mg preferably contains "c" atomic%, in a total amount, of at least one element selected from the group consisting of La, Ce, Pr, Eu and Mm, wherein "c" satisfy the following 15 expressions (4) and (5):

(4) $0 \leq c \leq 3.0$; and

(5) $0.2 \leq b+c \leq 6.0$.

Mm (misch metal) is a mixture or an alloy of a 20 number of rare-earth elements consisting of Ce and La mainly, and is a residue generated by refining and removing useful rare-earth element, such as Sm and Nd, from mineral ore. Its composition depends on a composition of the mineral ore before the refining.

In the high strength and high toughness magnesium 25 alloy according to the present invention, Mg preferably contains "c" atomic%, in a total amount, of at least one element selected from the group consisting of Yb, Tb, Sm

and Nd and "d" atomic%, in a total amount, of at least one element selected from the group consisting of La, Ce, Pr, Eu and Mm, wherein "c" and "d" satisfies the following expressions (4) to (6):

5 (4) $0 \leq c \leq 3.0$;
(5) $0 \leq d \leq 3.0$; and
(6) $0.2 \leq b+c+d \leq 6.0$.

A high strength and high toughness magnesium alloy according to the present invention preferably comprises 10 "a" atomic% of Zn, "b" atomic%, in a total amount, of at least one element selected from the group consisting of Dy, Ho and Er and a residue of Mg, wherein "a" and "b" satisfy the following expressions (1) to (3):

15 (1) $0.1 \leq a \leq 5.0$;
(2) $0.5 \leq b \leq 5.0$; and
(3) $0.5a - 0.5 \leq b$.

A high strength and high toughness magnesium alloy according to the present invention preferably comprises "a" atomic% of Zn, "b" atomic%, in a total amount, of at 20 least one element selected from the group consisting of Dy, Ho and Er and a residue of Mg, wherein "a" and "b" satisfy the following expressions (1) to (3):

25 (1) $0.1 \leq a \leq 3.0$;
(2) $0.1 \leq b \leq 5.0$; and
(3) $2a - 3 \leq b$.

And, in the high strength and high toughness magnesium alloy comprises a magnesium alloy casting

product to which a plastic working after cutting is subjected.

A high strength and high toughness magnesium alloy according to the present invention preferably comprises 5 a plastically worked product which is produced by preparing a magnesium alloy casting product containing "a" atomic% of Zn, "b" atomic%, in a total amount, of at least one element selected from the group consisting of Dy, Ho and Er and a residue of Mg, wherein "a" and "b" 10 satisfy the following expressions (1) to (3), cutting said magnesium alloy casting product to form a chip-shaped casting product and then solidifying said chip-shaped casting product by a plastic working, wherein said plastically worked product has a hcp structured 15 magnesium phase and a long period stacking ordered structure phase at room temperature:

- (1) $0.1 \leq a \leq 5.0$:
- (2) $0.1 \leq b \leq 5.0$: and
- (3) $0.5a - 0.5 \leq b$.

20 A high strength and high toughness magnesium alloy according to the present invention preferably comprises a plastically worked product which is produced by preparing a magnesium alloy casting product containing "a" atomic% of Zn, "b" atomic%, in a total amount, of at 25 least one element selected from the group consisting of Dy, Ho and Er and a residue of Mg, wherein "a" and "b" satisfy the following expressions (1) to (3), cutting

said magnesium alloy casting product to form a chip-shaped casting product and then solidifying said chip-shaped casting product by a plastic working, wherein said plastically worked product has a hcp structured 5 magnesium phase and a long period stacking ordered structure phase at room temperature:

- (1) $0.1 \leq a \leq 3.0$;
- (2) $0.1 \leq b \leq 5.0$; and
- (3) $2a - 3 \leq b$.

10 A high strength and high toughness magnesium alloy according to the present invention preferably comprises a plastically worked product which is produced by preparing a magnesium alloy casting product containing "a" atomic% of Zn, "b" atomic%, in a total amount, of at 15 least one element selected from the group consisting of Dy, Ho and Er and a residue of Mg, wherein "a" and "b" satisfy the following expressions (1) to (3), cutting said magnesium alloy casting product to form a chip-shaped casting product and then solidifying said chip-shaped casting product by a plastic working and a heat 20 treatment, wherein said plastically worked product has a hcp structured magnesium phase and a long period stacking ordered structure phase at room temperature:

- (1) $0.1 \leq a \leq 5.0$;
- (2) $0.1 \leq b \leq 5.0$; and
- (3) $0.5a - 0.5 \leq b$.

A high strength and high toughness magnesium alloy

according to the present invention preferably comprises a plastically worked product which is produced by preparing a magnesium alloy casting product containing "a" atomic% of Zn, "b" atomic%, in a total amount, of at least one element selected from the group consisting of Dy, Ho and Er and a residue of Mg, wherein "a" and "b" satisfy the following expressions (1) to (3), cutting said magnesium alloy casting product to form a chip-shaped casting product and then solidifying said chip-shaped casting product by a plastic working and a heat treatment, wherein said plastically worked product has a hcp structured magnesium phase and a long period stacking ordered structure phase at room temperature:

(1) $0.1 \leq a \leq 3.0$;

(2) $0.1 \leq b \leq 5.0$; and

(3) $2a - 3 \leq b$.

And, in the high strength and high toughness magnesium alloy according to the present invention, the hcp structured magnesium phase preferably has an average particle size of $0.1\mu\text{m}$ or more.

And, in the high strength and high toughness magnesium alloy according to the present invention, the long period stacking ordered structure phase preferably has at least single-digit smaller dislocation density than said hcp structured magnesium phase.

And, in the high strength and high toughness magnesium alloy according to the present invention, the

long period stacking ordered structure phase preferably has a crystal grain having a volume fraction of 5% or more.

And, in the high strength and high toughness 5 magnesium alloy according to the present invention, the plastically worked product preferably contains at least one kind of precipitation selected from the group consisting of a compound of Mg and rare-earth element, a compound of Mg and Zn, a compound of Zn and rare-earth 10 element and a compound of Mg, Zn and rare-earth element.

And, in the high strength and high toughness magnesium alloy according to the present invention, the at least one kind of precipitation preferably has a total volume fraction of larger than 0 to 40% or less.

15 And, in the high strength and high toughness magnesium alloy according to the present invention, the plastic working is preferably carried out by at least one process in a rolling, an extrusion, an ECAE working, a drawing, a forging, a press, a form rolling, a 20 bending, a FSW working and a cyclic working of theses workings.

And, in the high strength and high toughness magnesium alloy according to the present invention, a total strain amount when said plastic working is carried 25 out is preferably 15 or less.

And, in the high strength and high toughness magnesium alloy according to the present invention, a

total strain amount when said plastic working is carried out is preferably 10 or less.

And, in the high strength and high toughness magnesium alloy according to the present invention, Mg 5 may contains "y" atomic%, in a total amount, of Y and/or Gd, wherein "y" satisfies the following expressions (4) and (5):

$$(4) 0 \leq y \leq 4.9; \text{ and}$$

$$(5) 0.1 \leq b+y \leq 5.0.$$

10 And, in the high strength and high toughness magnesium alloy according to the present invention, Mg may contains "c" atomic%, in a total amount, of at least one element selected from the group consisting of Yb, Tb, Sm and Nd, wherein "c" satisfies the following 15 expressions (4) and (5):

$$(4) 0 \leq c \leq 3.0; \text{ and}$$

$$(5) 0.1 \leq b+c \leq 6.0.$$

And, in the high strength and high toughness magnesium alloy according to the present invention, Mg 20 may contains "c" atomic%, in a total amount, of at least one element selected from the group consisting of La, Ce, Pr, Eu and Mm, wherein "c" satisfies the following expressions (4) and (5):

$$(4) 0 \leq c \leq 3.0; \text{ and}$$

$$25 (5) 0.1 \leq b+c \leq 6.0.$$

And, in the high strength and high toughness magnesium alloy according to the present invention, Mg

may contains "c" atomic%, in a total amount, of at least one element selected from the group consisting of Yb, Tb, Sm and Nd and "d" atomic%, in a total amount, of at least one element selected from the group consisting of 5 La, Ce, Pr, Eu and Mm, wherein "c" and "d" satisfy the following expressions (4) to (6):

- (4) $0 \leq c \leq 3.0$;
- (5) $0 \leq d \leq 3.0$; and
- (6) $0.1 \leq b+c+d \leq 6.0$.

10 And, in the high strength and high toughness magnesium alloy according to the present invention, Mg may contains larger than 0 atomic% to 2.5 atomic% or less, in a total amount, of at least one element selected from the group consisting of Al, Th, Ca, Si, 15 Mn, Zr, Ti, Hf, Nb, Ag, Sr, Sc, B, C, Sn, Au, Ba, Ge, Bi, Ga, In, Ir, Li, Pd, Sb and V.

A method of producing a high strength and high toughness magnesium alloy according to the present invention preferably comprises:

20 a step for preparing a magnesium alloy casting product containing "a" atomic% of Zn, "b" atomic%, in a total amount, of at least one element selected from the group consisting of Dy, Ho and Er and a residue of Mg, wherein "a" and "b" satisfy the following expressions 25 (1) to (3), and

a step for producing a plastically worked product by subjecting said magnesium alloy casting product to a

plastic working:,

- (1) $0.2 \leq a \leq 5.0$;
- (2) $0.2 \leq b \leq 5.0$; and
- (3) $0.5a - 0.5 \leq b$.

5 According to the method of producing a high strength and high toughness magnesium alloy of the present invention, the plastic working for the magnesium alloy casting product can improve hardness and yield strength of the plastically worked product after the 10 plastic working as compared with the casting product before the plastic working.

And, the method of producing a high strength and high toughness magnesium alloy according to the present invention preferably may comprise a step for subjecting 15 the magnesium alloy casting product to a homogenized heat treatment between the step for preparing the magnesium alloy casting product and the step for producing the plastically worked product. In this case, the homogenized heat treatment is preferably carried out 20 under a condition of a temperature of 400°C to 550°C and a treating period of 1 minute to 1500 minutes.

In addition, the method of producing a high strength and high toughness magnesium alloy according to the present invention may further comprise a step for subjecting the plastically worked product to a heat treatment after the step for producing the plastically worked product. In this case, the heat treatment is 25

preferably carried out under a condition of a temperature of 150°C to 450°C and a treating period of 1 minute to 1500 minutes.

A method of producing a high strength and high 5 toughness magnesium alloy according to the present invention preferably comprises:

a step for preparing a magnesium alloy casting product containing "a" atomic% of Zn, "b" atomic%, in a total amount, of at least one element selected from the 10 group consisting of Dy, Ho and Er and a residue of Mg, wherein "a" and "b" satisfy the following expressions (1) to (3), and

a step for producing a plastically worked product by subjecting said magnesium alloy casting product to a 15 plastic working:

- (1) $0.2 \leq a \leq 3.0$;
- (2) $0.5 \leq b \leq 5.0$; and
- (3) $2a - 3 \leq b$.

And, in the method of producing a high strength and 20 high toughness magnesium alloy according to the present invention, the magnesium alloy casting product preferably has a hcp structured magnesium phase and a long period stacking ordered structure phase.

And, in the method of producing a high strength and 25 high toughness magnesium alloy according to the present invention, Mg may contains "c" atomic%, in a total amount, of at least one element selected from the group

consisting of Yb, Tb, Sm and Nd, wherein "c" satisfies the following expressions (4) and (5):

(4) $0 \leq c \leq 3.0$; and

(5) $0.2 \leq b+c \leq 6.0$.

5 And, in the method of producing a high strength and high toughness magnesium alloy according to the present invention, Mg contains "c" atomic%, in a total amount, of at least one element selected from the group consisting of La, Ce, Pr, Eu, Mm and Gd, wherein "c" 10 satisfies the following expressions (4) and (5):

(4) $0 \leq c \leq 3.0$; and

(5) $0.2 \leq b+c \leq 6.0$.

And, in the method of producing a high strength and high toughness magnesium alloy according to the present 15 invention, Mg contains "c" atomic%, in a total amount, of at least one element selected from the group consisting of Yb, Tb, Sm and Nd and "d" atomic%, in a total amount, of at least one element selected from the group consisting of La, Ce, Pr, Eu, Mm and Gd, wherein 20 "c" and "d" satisfy the following expressions (4) to (6):

(4) $0 \leq c \leq 3.0$;

(5) $0 \leq d \leq 3.0$; and

(6) $0.2 \leq b+c+d \leq 6.0$.

25 A method of producing a high strength and high toughness magnesium alloy according to the present invention preferably comprises:

a step for preparing a magnesium alloy casting product containing "a" atomic% of Zn, "b" atomic%, in a total amount, of at least one element selected from the group consisting of Dy, Ho and Er and a residue of Mg,
5 wherein "a" and "b" satisfy the following expressions (1) to (3);

a step for producing a chip-shaped casting product by cutting said magnesium alloy casting product; and

10 a step for producing a plastically worked product by solidifying said chip-shaped casting product by a plastic working:

(1) $0.1 \leq a \leq 5.0$;

(2) $0.1 \leq b \leq 5.0$; and

(3) $0.5a - 0.5 \leq b$.

15 A method of producing a high strength and high toughness magnesium alloy according to the present invention preferably comprises:

a step for preparing a magnesium alloy casting product containing "a" atomic% of Zn, "b" atomic%, in a total amount, of at least one element selected from the group consisting of Dy, Ho and Er and a residue of Mg,
20 wherein "a" and "b" satisfy the following expressions (1) to (3);

a step for producing a chip-shaped casting product by cutting said magnesium alloy casting product; and

a step for producing a plastically worked product by solidifying said chip-shaped casting product by a

plastic working:

- (1) $0.1 \leq a \leq 3.0$;
- (2) $0.1 \leq b \leq 5.0$; and
- (3) $2a - 3 \leq b$.

5 And, in the method of producing a high strength and high toughness magnesium alloy according to the present invention, the magnesium alloy casting product preferably has a hcp structured magnesium phase and a long period stacking ordered structure phase.

10 And, in the method of producing a high strength and high toughness magnesium alloy according to the present invention, Mg may contains "c" atomic%, in a total amount, of at least one element selected from the group consisting of Yb, Tb, Sm and Nd, wherein "c" satisfies 15 the following expressions (4) and (5):

- (4) $0 \leq c \leq 3.0$; and
- (5) $0.1 \leq b+c \leq 6.0$.

20 And, in the method of producing a high strength and high toughness magnesium alloy according to the present invention, Mg contains "c" atomic%, in a total amount, of at least one element selected from the group consisting of La, Ce, Pr, Eu, Mm and Gd, wherein "c" satisfies the following expressions (4) and (5):

- (4) $0 \leq c \leq 3.0$; and
- 25 (5) $0.1 \leq b+c \leq 6.0$.

And, in the method of producing a high strength and high toughness magnesium alloy according to the present

invention, Mg may contains "c" atomic%, in a total amount, of at least one element selected from the group consisting of Yb, Tb, Sm and Nd and "d" atomic%, in a total amount, of at least one element selected from the 5 group consisting of La, Ce, Pr, Eu, Mm and Gd, wherein "c" and "d" satisfy the following expressions (4) to (6):

- (4) $0 \leq c \leq 3.0$;
- (5) $0 \leq d \leq 3.0$; and
- 10 (6) $0.1 \leq b+c+d \leq 6.0$.

And, in the method of producing a high strength and high toughness magnesium alloy according to the present invention, Mg may contains larger than 0 atomic% to 2.5 atomic% or less, in a total amount, of at least one 15 element selected from the group consisting of Al, Th, Ca, Si, Mn, Zr, Ti, Hf, Nb, Ag, Sr, Sc, B, C, Sn, Au, Ba, Ge, Bi, Ga, In, Ir, Li, Pd, Sb and V.

And, in the method of producing a high strength and high toughness magnesium alloy according to the present 20 invention, the plastic working is carried out by at least one process in a rolling, an extrusion, an ECAE working, a drawing, a forging, a press, a form rolling, a bending, a FSW working and a cyclic working of theses workings.

25 In the method of producing a high strength and high toughness magnesium alloy according to the present invention, a total strain amount when the plastic

working is carried out is preferably 15 or less, more preferably, 10 or less. And, a strain amount per one of the plastic working is preferably 0.002 to 4.6.

The total strain amount means a total strain amount 5 which is not canceled by a heat treatment such as annealing. In other words, a strain amount which is canceled by a heat treatment during a producing procedure is not contained in the total strain amount.

However, in a case of a high strength and high 10 toughness magnesium alloy produced by a step for producing a chip-shaped casting product, the total strain amount means a total strain amount when a plastic working is carried out after producing a product prepared for a final solidifying-forming. So, a strain 15 amount generated before producing a product prepared to a final solidifying-forming is not contained in the total strain amount. The product prepared to the final solidifying-forming is a product having less bonding strength of chips and having a tensile strength of 20 200MPa and below. The solidifying-forming of the chip-shaped casting product is carried out by any process of an extrusion, a rolling, a forging, a press, an ECAE working and the like. After the solidifying-forming, a rolling, an extrusion, an ECAE working, a drawing, a 25 forging, a press, a form rolling, a bending and a FSW working may be applied. And, before the final solidifying-forming, the chip-shaped casting product may

be subjected to various plastic working such as a ball milling, a cyclic forming and a stamping milling.

The method of producing a high strength and high toughness magnesium alloy according to the present invention may further comprise a step for heat-treating the plastically worked product after the step for producing the plastically worked product. As a result, the plastically worked product can be improved in hardness and yield strength compared with the product before the heat treatment.

In the method of producing a high strength and high toughness magnesium alloy according to the present invention, the heat treatment is preferably carried out under a condition of a temperature of 200°C to lower than 500°C and a treating period of 10 minutes to shorter than 24 hours.

And, in the method of producing a high strength and high toughness magnesium alloy according to the present invention, the magnesium alloy after subjecting to the plastic working has a hcp structured phase preferably having single-digit larger dislocation density than a long period stacking ordered structure phase.

Effect of the Invention

As mentioned above, the present invention can provide a high strength and high toughness magnesium alloy having a strength and a toughness both being on a

sufficient level for an alloy to be practically used for expanded applications of a magnesium alloy.

Detailed Description of Embodiment of the Invention

Hereinafter, preferred embodiments of the present 5 invention will be described.

The inventors, back to basics, have studied a strength and a toughness of a binary magnesium alloy at the first step. Then, the study is expanded to a multi-element magnesium alloy. As a result, it is found that a 10 magnesium alloy having a sufficient strength and toughness property is a Mg-Zn-RE (rare-earth element) based magnesium alloy. The rare-earth element is at least one element selected from the group consisting of Y, Dy, Ho and Er. In addition, it is also found that 15 when a magnesium alloy contains Zn and Re in a small amount as 5.0 atomic% or less, respectively, unlike in conventional technique, a nonconventional high strength and high toughness property can be obtained.

Furthermore, it is found that subjecting a casting 20 alloy, which forms a long period stacking ordered structure phase, to a plastic working or to a heat treatment after a plastic working can provide a high strength, high ductile and high toughness magnesium alloy. In addition, an alloy composition capable of 25 forming a long period stacking ordered structure and providing a high strength, high ductile and high toughness property by subjecting to a plastic working or

to a heat treatment after a plastic working can be also found.

Beside, it is also found that by producing a chip-shaped casting product by cutting a casting alloy, which 5 forms a long period stacking ordered structure, and then subjecting the chip-shaped casting product to a plastic working or a heat treating after a plastic working, a higher strength, higher ductile and higher toughness magnesium alloy can be obtained as compared with a case 10 not containing the step for cutting into a chip-shaped casting product. And, an alloy composition can be found, which can form a long period stacking ordered structure and provide a high strength, high ductile and high toughness property after subjecting a chip-shaped 15 casting product to a plastic working or to a heat treatment after a plastic working.

A plastic working for a metal having a long period stacking ordered structure phase allows flexing or bending at least a part of the long period stacking 20 ordered structure phase. As a result, a high strength, high ductile and high toughness metal can be obtained.

The flexed or bent long period stacking ordered structure phase has a random grain boundary. It is thought that the random grain boundary strengthens a 25 magnesium alloy and suppresses a grain boundary sliding, resulting in obtaining a high strength property at high temperatures.

And, it is probable that a high density dislocation of a hcp structured magnesium phase strengthens a magnesium alloy; while a small density dislocation of a long period stacking ordered structure phase improves 5 ductility and strength of the magnesium alloy. And, the long period stacking ordered structure phase preferably has at least single-digit smaller dislocation density than the hcp structured magnesium phase.

(Embodiment 1)

10 A magnesium alloy according to the first embodiment of the present invention is a ternary or more alloy essentially containing Mg, Zn and rare-earth element, wherein the rare-earth element is one or two or more elements selected from the group consisting of Dy, Ho 15 and Er.

A composition range of the Mg alloy according to the embodiment is shown in Fig.8 at a range bounded by a line of A-B-C-D-E. When a content of Zn is set to "a" atomic% and a content of one or more rare-earth elements 20 is set to "b" atomic%, "a" and "b" satisfy the following expressions (1) to (3):

- (1) $0.2 \leq a \leq 5.0$;
- (2) $0.2 \leq b \leq 5.0$; and
- (3) $0.5a - 0.5 \leq b$.

25 When a rare-earth element is one or more elements selected from the group consisting of Dy, Ho and Er, the magnesium alloy may further contain "y" atomic%, in a

total amount, of Y and/or Gd, wherein "y" preferably satisfies the following expressions (4) and (5):

$$(4) 0 \leq y \leq 4.8 \text{ and}$$

$$(5) 0.2 \leq b+y \leq 5.0.$$

5 When a content of Zn exceeds 5 atomic%, a toughness (a ductility) tends to deteriorate particularly. And, when a total content of one or two or more rare-earth elements exceed 5 atomic%, a toughness (a ductility) tends to deteriorate particularly.

10 In addition, when a content of Zn is less than 0.3 atomic% or a total content of the rare-earth elements is less than 0.2 atomic%, either one of strength or toughness deteriorates. Accordingly, a lower limit of a content of Zn is set to 0.2 atomic% and a lower limit of 15 a total content of rare-earth elements is set to 0.2 atomic%.

When a content of Zn is 0.2 to 1.5 atomic%, a strength and a toughness are remarkably increased. In a case of a content of Zn of near 0.2 atomic%, although a 20 strength tends to decrease when a content of rare-earth element decreases, the strength and the toughness can be maintained at a higher level than that of a conventional alloy. Accordingly, in a magnesium alloy according to the embodiment, a content of Zn is set to a maximum 25 range within 0.2 atomic% to 5.0 atomic%.

In a Mg-Zn-Y based magnesium alloy according to the present invention, a residue other than Zn and the rare-

earth element within the aforesaid amount range is magnesium; however, the magnesium alloy may contain impurities of such a content that characteristics of the alloy is not influenced.

5 When the rare-earth element is one or more elements selected from the group consisting of Dy, Ho and Er, a composition of the magnesium alloy satisfies the aforesaid expressions (1) to (3); however, preferably satisfies the following expressions (1') to (3'):

10 (1') $0.2 \leq a \leq 3.0$;
(2') $0.2 \leq b \leq 5.0$; and
(3') $2a-3 \leq b$.

(Embodiment 2)

A magnesium alloy according to the second
15 embodiment of the present invention is a quaternary
alloy or more alloy essentially containing Mg, Zn and
rare-earth element, wherein the rare-earth element is
one or two or more elements selected from the group
consisting of Dy, Ho and Er and the forth element is one
20 or two or more elements selected from the group
consisting of Yb, Tb, Sm and Nd.

In a composition range of the Mg alloy according to
the embodiment, when a content of Zn is set to "a"
atomic%, a total content of one or two or more rare-
25 earth element is set to "b" atomic% and a total content
of one or two or more forth elements is set to "c"
atomic%, "a", "b" and "c" satisfy the following

expressions (1) to (5):

- (1) $0.2 \leq a \leq 5.0$;
- (2) $0.2 \leq b \leq 5.0$;
- (3) $0.5a - 0.5 \leq b$;
- 5 (4) $0 \leq c \leq 3.0$; and
- (5) $0.2 \leq b+c \leq 6.0$.

Causes setting a content of Zn to 5 atomic% or less, setting a total content of one or two or more rare-earth elements to 5 atomic% or less, setting a 10 content of Zn to 0.2 atomic% or more and setting a total amount of the rare-earth elements to 0.2 atomic% or more are the same as Embodiment 1. In this embodiment, an upper limit of a content of the forth element is set to 3.0 atomic% because the forth element has a small solid 15 solubility limit. And, the reason for containing the forth element is because of effects for forming a fine-grained structure and for precipitating an intermetallic compound.

The Mg-Zn-Y base magnesium alloy according to the 20 embodiment may contain impurities at such a content that characteristics of the alloy is not influenced.

When the rare-earth element is one or more elements selected from the group consisting of Dy, Ho and Er, a 25 composition of the magnesium alloy satisfies the aforesaid expressions (1) to (5); however, preferably satisfies the following expressions (1') to (5'):

- (1') $0.2 \leq a \leq 3.0$;

(2') $0.2 \leq b \leq 5.0$;

(3') $2a-3 \leq b$;

(4') $0 \leq c \leq 3.0$; and

(5') $0.2 \leq b+c \leq 6.0$.

5 (Embodiment 3)

A magnesium alloy according to the third embodiment of the present invention is a quaternary alloy or more alloy essentially containing Mg, Zn and rare-earth element, wherein the rare-earth element is one or two or 10 more elements selected from the group consisting of Dy, Ho and Er and the forth element is one or two or more elements selected from the group consisting of La, Ce, Pr, Eu, Mm and Gd. Mm (misch metal) is a mixture or an alloy of a number of rare-earth elements consisting of 15 Ce and La mainly, and is a residue generated by refining and removing useful rare-earth element, such as Sm and Nd, from a mineral ore. Its composition depends on a composition of the mineral ore before the refining.

In a composition range of the Mg alloy according to 20 the embodiment, when a content of Zn is set to "a" atomic%, a total content of one or two or more rare-earth elements is set to "b" atomic% and a total content of one or two or more forth elements is set to "c" atomic%, "a", "b" and "c" satisfy the following 25 expressions (1) to (5):

(1) $0.2 \leq a \leq 5.0$;

(2) $0.2 \leq b \leq 5.0$;

(3) $0.5a - 0.5 \leq b$;

(4) $0 \leq c \leq 3.0$; and

(5) $0.2 \leq b + c \leq 6.0$.

Causes setting a content of Zn to 5 atomic% or 5 less, setting a total content of one or two or more rare-earth elements to 5 atomic% or less, setting a content of Zn to 0.2 atomic% or more and setting a total amount of the rare-earth elements to 0.2 atomic% or more are the same as Embodiment 1. In this embodiment, an 10 upper limit of a content of the forth element is set to 3.0 atomic% because the forth element has a small solid solubility limit. And, the reason for containing the forth element is because of effects for forming a fine-grained structure and for precipitating an intermetallic 15 compound.

The Mg-Zn-Y base magnesium alloy according to the embodiment may contain impurities at such a content that characteristics of the alloy is not influenced.

When the rare-earth element is one or more elements 20 selected from the group consisting of Dy, Ho and Er, a composition of the magnesium alloy satisfies the aforesaid expressions (1) to (5); however, preferably satisfies the following expressions (1') to (5'):

(1') $0.2 \leq a \leq 3.0$;

25 (2') $0.2 \leq b \leq 5.0$;

(3') $2a - 3 \leq b$;

(4') $0 \leq c \leq 3.0$; and

(5') $0.2 \leq b+c \leq 6.0$.

(Embodiment 4)

A magnesium alloy according to the forth embodiment of the present invention is a quintet alloy or more 5 alloy essentially containing Mg, Zn and rare-earth element, wherein the rare-earth element is one or two or more elements selected from the group consisting of Dy, Ho and Er, the forth element is one or two or more elements selected from the group consisting of Yb, Tb, 10 Sm and Nd and the fifth element is one or two or more elements selected from the group consisting of La, Ce, Pr, Eu, Mm and Gd.

In a composition range of the Mg alloy according to the embodiment, when a content of Zn is set to "a" 15 atomic%, a total content of one or two or more rare-earth elements is set to "b" atomic%, a total content of one or two or more forth elements is set to "c" atomic% and a total content of one or two or more fifth elements is set to "d" atomic%, "a", "b", "c" and "d" satisfy the 20 following expressions (1) to (6):

(1) $0.2 \leq a \leq 5.0$;

(2) $0.2 \leq b \leq 5.0$;

(3) $0.5a - 0.5 \leq b$;

(4) $0 \leq c \leq 3.0$;

25 (5) $0 \leq d \leq 3.0$; and

(6) $0.2 \leq b+c+d \leq 6.0$.

The reason for setting a total content of the rare-

earth element, the forth element and the fifth element to 6.0 atomic% or less is because the alloy increases in weight, a raw material cost increases and a toughness decreases if the total content exceeds 6 atomic%. The 5 reason for setting a total content of the rare-earth element, the forth element and the fifth element to 0.2 atomic% or more is because the strength deteriorates if the total content is less than 0.2 atomic%. And, the reason for containing the forth and the fifth elements 10 is because of effects for forming a fine-grained structure and for precipitating an intermetallic compound.

The Mg-Zn-Y base magnesium alloy according to the embodiment may contain impurities at such a content that 15 characteristics of the alloy is not influenced.

When the rare-earth element is one or two or more elements selected from the group consisting of Dy, Ho and Er, a composition of the magnesium alloy satisfies the aforesaid expressions (1) to (6); however, 20 preferably satisfies the following expressions (1') to (6'):

$$(1') 0.2 \leq a \leq 3.0;$$

$$(2') 0.2 \leq b \leq 5.0;$$

$$(3') 2a-3 \leq b;$$

$$25 (4') 0 \leq c \leq 3.0;$$

$$(5') 0 \leq d \leq 3.0; \text{ and}$$

$$(6') 0.2 \leq b+c+d \leq 6.0.$$

(Embodiment 5)

A magnesium alloy according to the fifth embodiment of the present invention is a magnesium alloy having any compositions of the magnesium alloys described in the Embodiment 1 to 4 to which Me is added. Me is at least one element selected from the group consisting of Al, Th, Ca, Si, Mn, Zr, Ti, Hf, Nb, Ag, Sr, Sc, B, C, Sn, Au, Ba, Ge, Bi, Ga, In, Ir, Li, Pd, Sb and V. A content of Me is set to 0 atomic% to 2.5 atomic%. A content of Me is set to larger than 0 atomic% to 2.5 atomic% or less. An addition of Me can improve characteristics other than the strength and the toughness which are being kept high. For instance, a corrosion resistance and an effect for forming a fine-grained crystal structure are improved.

(Embodiment 6)

A method of producing a magnesium alloy according to the sixth embodiment of the present invention will be described.

A magnesium alloy having any one composition in the magnesium alloys according to the Embodiments 1 to 5 was melted and cast to prepare a magnesium alloy casting product. A cooling rate at the casting was 1000K/sec or less, more preferably 100K/sec or less. The casting process may employ various process, such as a high-pressure cast process, a roll cast process, a tilting cast process, a continuous cast process, a thixocasting

process, a die casting process and the like. And, the magnesium alloy casting product may be cut into a specified shape for employing.

Next, the magnesium alloy casting product may be 5 subjected to a homogenized heat treatment. In this case, a heating temperature is preferably 400°C to 550°C and a treating period is preferably 1 minute to 1500 minutes (or 24 hours).

Then, the magnesium alloy casting product was 10 plastically worked. As the plastic working method, an extrusion, an ECAE (Equal Channel Angular Extrusion) working method, a rolling, a drawing, a forging, a press, a form rolling, a bending, a FAW (Friction Stir Welding) working, a cyclic process thereof and the like 15 may be employed.

When the plastic working method is an extrusion, an extrusion temperature is preferably set to 250°C to 500°C and a reduction rate of a cross section due to the extrusion is preferably set to be 5% or more.

20 The ECAE working is carried out such that a sample is rotated every 90° in the length direction thereof every pass for introducing a strain therein uniformly. Specifically, a forming die having a forming pore of a 25 L-shaped cross section is employed, and the magnesium alloy casting product as a forming material is forcibly poured in the forming pore. And, the magnesium alloy casting product is applied with stress at a portion at

which the L-shaped forming pore is curved at 90° thereby to obtain a compact excellent in strength and toughness. A number of passes of the ECAE working is preferably set to 1 to 8, more preferably, 3 to 5. A temperature of the 5 ECAE working is preferably set to 250°C to 500°C.

When the plastic working method is an extrusion, an extrusion temperature is preferably set to 250°C to 500°C and a rolling reduction is preferably set to 5% or more.

When the plastic working method is a drawing, a 10 drawing temperature is preferably set to 250°C to 500°C and a reduction rate of a cross section is preferably set to 5% or more.

When the plastic working method is a forging, a forging temperature is preferably set to 250°C to 500°C 15 and a processing rate is preferably set to 5% or more.

The plastic working for the magnesium alloy casting product is carried out such that an amount of strain per one working is preferably 0.002 to 4.6 and a total amount of strain is preferably 15 or less. More 20 preferably, an amount of strain per one working is 0.002 to 4.6 and a total amount of strain is 10 or less.

In the ECAE working, an amount of strain per one working is 0.95 to 1.15. So, when the ECAE working is carried out for 16 times, a total amount of strain is 25 added up to 15.2 (0.95×16). When the ECAE working is carried out for 8 times, a total amount of strain is added up to 7.6 (0.95×16).

In the extrusion, an amount of strain per one working is 0.92; 1.39; 2.30; 2.995; 3.91; 4.61 and 6.90 in a case of an extrusion rate of 2.5; 4; 10; 20; 50; 100 and 1000.

5 The aforesaid plastically worked product produced by subjecting the magnesium alloy casting product to a plastic working has a crystal structure of a hcp structured magnesium phase and a long period stacking ordered structure phase at room temperatures. And, the
10 long period stacking ordered structure has a crystal grain having a volume fraction of 5% or more (preferably, 10% or more). And, the hcp structured magnesium phase has an average particle diameter of $2\mu\text{m}$ or more and the long period stacking ordered structure phase has an average particle diameter of $0.2\mu\text{m}$ or more.
15 The long period stacking ordered structure phase has a number of random grain boundaries contained in crystal grain thereof. And, the crystal grain defined by the grain boundary has an average particle diameter of
20 $0.05\mu\text{m}$ or more. Although a dislocation density is large at the random grain boundary, a dislocation density is small at portions other than the random grain boundary in the long period stacking ordered structure phase.
Accordingly, the hcp structured magnesium phase has
25 single-digit larger dislocation density than portions other than the grain boundaries of the long period stacking ordered structure phase.

At least a part of the long period stacking ordered structure phase is flexed or bend. And, the plastically worked product may contain at least one kind of precipitation selected from the group consisting of a 5 compound of Mg and rare-earth element, a compound of Mg and Zn, a compound of Zn and rare-earth element and a compound of Mg, Zn and rare-earth element. The precipitation preferably has a total volume fraction of higher than 0 to 40% and below. And, the plastically 10 worked product has a hcp structured magnesium phase. The plastically worked product subjected to the plastic working is improved in Vickers hardness and yield strength as compared with the casting product before the plastic working.

15 The plastically worked product after subjecting to the plastic working may be subjected to a heat treatment. The heat treatment is preferably carried out at a temperature of 200°C or more to lower than 500°C and a treating period of 10 minutes to 1500 minutes (or 24 20 hours). The reason that the heating temperature is set to lower than 500°C is that an amount of strain applied by the plastic working is canceled if the temperature is 500°C or more.

The plastically worked product subjected to the 25 heat treatment is improved in Vickers hardness and yield strength as compared with that before the heat treatment. The plastically worked product after the heat

treatment, with as that before the heat treatment, has a crystal structure of a hcp structured magnesium phase and a long period stacking ordered structure phase at room temperatures. And, the long period stacking ordered 5 structure has a crystal grain having a volume fraction of 5% or more (preferably 10% or more). And, the hcp structured magnesium phase has an average particle diameter of $2\mu\text{m}$ or more and the long period stacking ordered structure phase has an average particle diameter 10 of $0.2\mu\text{m}$ or more. The long period stacking ordered structure phase has a number of random grain boundaries contained in crystal grain thereof. And, the crystal grain defined by the grain boundary has an average particle diameter of $0.05\mu\text{m}$ or more. Although a 15 dislocation density is large at the random grain boundaries, a dislocation density is small at portions other than the random grain boundary in the long period stacking ordered structure phase. Accordingly, a hcp structured magnesium phase has single-digit larger 20 dislocation density than that of portions other than the grain boundaries of the long period stacking ordered structure phase.

At least a part of the long period stacking ordered structure phase is flexed or bend. And, the plastically 25 worked product may contain at least one kind of precipitation selected from the group consisting of a compound of Mg and rare-earth element, a compound of Mg

and Zn, a compound of Zn and rare-earth element and a compound of Mg, Zn and rare-earth element. The precipitation preferably has a total volume fraction of higher than 0 to 40% and below.

5 According to the Embodiments 1 to 6, a high strength and high toughness magnesium alloy having a strength and a toughness both being on a level for an alloy to be practically used for expanded applications of a magnesium alloy, for example, a high technology 10 alloy requiring a high strength and toughness, and a method of producing the same can be provided.

(Embodiment 7)

A magnesium alloy according to the seventh 15 embodiment is applied for a number of chip-shaped casting products each having a side length of several mm or less on a side produced by cutting a casting product. The magnesium alloy is a ternary or quaternary or more 20 alloy essentially containing Mg, Zn and rare-earth element, wherein the rare-earth element is one or two or more elements selected from the group consisting of Dy, Ho and Er.

A composition range of the alloy according to the embodiment is shown in Fig.9 at a range bounded by a 25 line of A-B-C-D-E. When a content of Zn is set to "a" atomic% and a total content of one or two or more rare-earth elements is set to "b" atomic%, "a" and "b"

satisfy the following expressions (1) to (3):

- (1) $0.1 \leq a \leq 5.0$,
- (2) $0.1 \leq b \leq 5.0$ and
- (3) $0.5a - 0.5 \leq b$.

5 When the rare-earth element is one or more elements selected from the group consisting of Dy, Ho and Er, the magnesium alloy may further contain "y" atomic%, in a total amount, of Y and/or Gd, wherein "y" satisfies the following expressions (4) and (5):

10 (4) $0 \leq y \leq 4.9$; and

(5) $0.1 \leq b + y \leq 5.0$.

When a content of Zn exceeds 5 atomic%, a toughness (or a ductility) tends to decrease particularly. And, when a content of one or two or more rare-earth elements 15 exceed 5 atomic%, a toughness (a ductility) tends to decrease particularly.

And, when a content of Zn is less than 0.1 atomic% or a total content of the rare-earth elements is less than 0.1 atomic%, either one of strength or toughness 20 deteriorates. Accordingly, a lower limit of a content of Zn is set to 0.1 atomic% and a lower limit of a content of the rare-earth element is set to 0.1 atomic%. The reason that each of the lower limits of the contents of Zn and the rare-earth element can be decreased to half 25 of that of the first embodiment is for employing the chip-shaped casting products.

When a content of Zn is 0.5 to 1.5 atomic%, a

strength and a toughness are increased remarkably. In a case of a content of Zn of near 0.5 atomic%, although a strength tends to deteriorate when a content of rare-earth element decreases, the strength and the toughness 5 can be maintained at a higher level than a conventional alloy. Accordingly, in a magnesium alloy according to the embodiment, a content of Zn is set to a maximum range within 0.1 atomic% to 5.0 atomic%.

The Mg-Zn-RE base magnesium alloy according to the 10 embodiment may contain impurities at such content that characteristics of the alloy is not influenced.

When the rare-earth element is one or two or more elements selected from the group consisting of Dy, Ho and Er, a composition of the magnesium alloy satisfies 15 the aforesaid expressions (1) to (3); however, preferably satisfies the following expressions (1') to (3'):

$$(1') 0.1 \leq a \leq 3.0;$$

$$(2') 0.1 \leq b \leq 5.0; \text{ and}$$

$$20 (3') 2a-3 \leq b.$$

(Embodiment 8)

A magnesium alloy according to the eighth embodiment is applied for a number of chip-shaped casting products each having a side length of several mm 25 or less produced by cutting a casting product. The magnesium alloy is a quaternary or more alloy essentially containing Mg, Zn and rare-earth element,

wherein the rare-earth element is one or two or more elements selected from the group consisting of Dy, Ho and Er and the forth element is one or two or more elements selected from the group consisting of Yb, Tb, 5 Sm and Nd.

In a composition range of the alloy according to the embodiment, when a content of Zn is set to "a" atomic% and a total content of one or two or more rare-earth elements is set to "b" atomic% and a total content 10 of the forth elements is set to "c" atomic%, "a", "b" and "c" satisfy the following expressions (1) to (5):

- (1) $0.1 \leq a \leq 5.0$;
- (2) $0.1 \leq b \leq 5.0$;
- (3) $0.5a - 0.5 \leq b$;
- 15 (4) $0 \leq c \leq 3.0$; and
- (5) $0.1 \leq b+c \leq 6.0$.

The Mg-Zn-RE base magnesium alloy according to the embodiment may contain impurities at such a content that characteristics of the alloy is not influenced.

20 When the rare-earth element is one or two or more elements selected from the group consisting of Dy, Ho and Er, a composition of the magnesium alloy satisfies the aforesaid expressions (1) to (3); however, preferably satisfies the following expressions (1') to 25 (3'):

- (1') $0.1 \leq a \leq 3.0$;
- (2') $0.1 \leq b \leq 5.0$; and

(3') $2a-3 \leq b$.

(Embodiment 9)

A magnesium alloy according to the ninth embodiment is applied for a number of chip-shaped casting products 5 each having a side length of several mm or less produced by cutting a casting product. The magnesium alloy is a quaternary or quintet or more alloy essentially containing Mg, Zn and rare-earth element, wherein the rare-earth element is one or two or more elements 10 selected from the group consisting of Dy, Ho and Er and the forth element is one or two or more elements selected from the group consisting of La, Ce, Pr, Eu, Mm and Gd.

In a composition range of the alloy according to 15 the embodiment, when a content of Zn is set to "a" atomic%, a total content of one or two or more rare-earth element is set to "b" atomic% and a total content of one or two or more forth elements is set to "c" atomic%, "a", "b" and "c" satisfy the following 20 expressions (1) to (5):

- (1) $0.1 \leq a \leq 5.0$;
- (2) $0.1 \leq b \leq 5.0$;
- (3) $0.5a-0.5 \leq b$;
- (4) $0 \leq c \leq 3.0$; and
- 25 (5) $0.1 \leq b+c \leq 6.0$.

Causes for setting a content of Zn to 5 atomic % or less, setting a total content of the one or two or more

rare-earth elements to 5 atomic% or less, setting a content of Zn to 0.1 atomic% or more and setting a total content of the rare-earth elements to 0.1 atomic% or more are the same as Embodiment 7. The reason for 5 setting an upper limit of a total content of the forth element to 3.0 atomic% is because the forth element has a little solid solubility limit. And, the reason for containing the forth element is because of effects for forming a fine-grained structure and for precipitating 10 an intermetallic compound.

The Mg-Zn-RE base magnesium alloy according to the embodiment may contain impurities at such a content that characteristics of the alloy is not influenced.

When the rare-earth element is one or two or more 15 elements selected from the group consisting of Dy, Ho and Er, a composition of the magnesium alloy satisfies the aforesaid expressions (1) to (3); however, preferably satisfies the following expressions (1') to (3'):

20 (1') $0.1 \leq a \leq 3.0$;
(2') $0.1 \leq b \leq 5.0$; and
(3') $2a-3 \leq b$.

(Embodiment 10)

A magnesium alloy according to the tenth embodiment 25 is applied for a number of chip-shaped casting products each having a side length of several mm or less produced by cutting a casting product. The magnesium alloy is a

quintet or more alloy essentially containing Mg, Zn and rare-earth element, wherein the rare-earth element is one or two or more elements selected from the group consisting of Dy, Ho and Er, the forth element is one or 5 two or more elements selected from the group consisting of Yb, Tb, Sm, Nd and Gd and the fifth element is one or two or more elements selected from the group consisting of La, Ce, Pr, Eu and Mm.

In a composition range of the alloy according to 10 the embodiment, when a content of Zn is set to "a" atomic% and a total content of one or two or more rare-earth elements is set to "b" atomic%, a total content of the one or two or more forth elements is set to "c" atomic% and a total content of the one or more fifth 15 elements is set to "d" atomic%, "a", "b", "c" and "d" satisfy the following expressions (1) to (6):

- (1) $0.1 \leq a \leq 5.0$;
- (2) $0.1 \leq b \leq 5.0$;
- (3) $0.5a - 0.5 \leq b$;
- 20 (4) $0 \leq c \leq 3.0$;
- (5) $0 \leq d \leq 3.0$; and
- (6) $0.1 \leq b + c + d \leq 6.0$.

Causes for setting a content of the rare-earth element and the forth and fifth elements to less than 25 6.0 atomic % and setting a total content of the rare-earth element and the forth and fifth element to larger than 0.1 atomic% are the same as Embodiment 4.

The Mg-Zn-RE base magnesium alloy according to the embodiment may contain impurities at such a content that characteristics of the alloy is not influenced.

When the rare-earth element is one or two or more 5 elements selected from the group consisting of Dy, Ho and Er, a composition of the magnesium alloy satisfies the aforesaid expressions (1) to (3); however, preferably satisfies the following expressions (1') to (3'):

10 (1') $0.1 \leq a \leq 3.0$;
(2') $0.1 \leq b \leq 5.0$; and
(3') $2a-3 \leq b$.

(Embodiment 11)

A magnesium alloy according to the eleventh 15 embodiment of the present invention is a magnesium alloy having any composition of the magnesium alloys described in the Embodiments 7 to 11 to which Me is added. Me is at least one element selected from the group consisting of Al, Th, Ca, Si, Mn, Zr, Ti, Hf, Nb, Ag, Sr, Sc, B, C, 20 Sn, Au, Ba, Ge, Bi, Ga, In, Ir, Li, Pd, Sb and V. A content of Me is set to larger than 0 atomic% to 2.5 atomic% or less. An addition of Me can improve characteristics other than the strength and the toughness which are being kept high. For instance, a 25 corrosion resistance and an effect for forming fine-grained crystal structure are improved.

(Embodiment 12)

A method of producing a magnesium alloy according to the twelve embodiment of the present invention will be described.

A magnesium alloy having any composition in the 5 magnesium alloys according to Embodiments 7 to 11 was melted and cast to prepare a magnesium alloy casting product. A cooling rate at the casting was 1000K/sec or less, more preferably 100K/sec or less. For the magnesium alloy casting product, products cut from ingot 10 into a specified shape was employed.

Next, the magnesium alloy casting product may be subjected to a homogenized heat treatment. In this case, a heating temperature is preferably set to 400°C to 550°C and a treating period is preferably set to 1 minute to 15 1500 minutes (or 24 hours).

Then, the magnesium alloy casting product was cut into a number of chip-shaped casting products each having a side length of several mm or less.

And, the chip-shaped casting products may be 20 preformed by a press or a plastic working method and then subjected to a homogenized heat treatment. In this case, a heating temperature is preferably set to 400°C to 550°C and a treating period is preferably set to 1 minute to 1500 minutes (or 24 hours). And, the preformed 25 product may be subjected to a heat treatment under a condition of a temperature of 150°C to 450°C and a treating period of 1 minute to 1500 minutes (or 24

hours).

The chip-shaped casting products are usually employed as a material for thixocasting.

And, a mixture of the chip-shaped casting product 5 and ceramic particles may be preformed by a press or a plastic working and then subjected to a homogenized heat treatment. And, before the performing of the chip-shaped casting products, a forced straining working may be carried out additionally.

10 Then, the chip-shaped casting products were plastically worked for solidifying-forming. For a method of the plastic working, various methods may be employed as with the Embodiment 6. And, before the solidifying-forming of the chip-shaped casting products, a cyclic 15 working such as a mechanical alloying, such as a ball milling and a stamp milling, and a bulk mechanical alloying may be applied. And, after the solidifying-forming, a plastic working or a blast working may be further carried out. And, the magnesium alloy casting 20 product may be combined with intermetallic compound particle, ceramic particle and fiber. And, the chip-shaped casting products may be mixed with ceramic particle and fiber.

The plastically worked product subjected to the 25 plastic working has a crystal structure of a hcp structured magnesium phase and a long period stacking ordered structure phase at room temperatures. At least a

part of the long period stacking ordered structure phase is flexed or bend. The plastically worked product subjected to the plastic working is improved in Vickers hardness and yield strength as compared with the casting 5 product before the plastic working.

A total amount of strain when the chip-shaped casting products are subjected to a plastic working is preferably 15 or less, more preferably, 10 or less. And, an amount of strain per one working is preferably 0.002 10 to 4.6.

The total strain amount means a total strain amount which is not canceled by a heat treatment such as annealing. Thus, it means a total amount of strain generated when the plastic working is carried out after 15 the performing the chip-shaped casting products. In other words, a strain amount which is canceled by a heat treatment during a producing procedure is not contained in the total amount. And, an amount of strain generated before performing the chip-shaped casting products is 20 not contained in the total amount.

The plastically worked product after subjecting the chip-shaped casting product to the plastic working may be subjected to a heat treatment. The heat treatment is preferably carried out at a temperature of 200°C or more 25 to lower than 500°C and a treating period of 10 minutes to 1500 minutes (or 24 hours). The reason for setting the heating temperature to lower than 500°C is that an

amount of strain applied by the plastic working is canceled if the temperature is 500°C or more.

The plastically worked product subjected to the heat treatment is improved in Vickers hardness and yield strength as compared with that before the heat treatment. And, the plastically worked product subjected to the heat treatment, as with that before the heat treatment, has a crystal structure of a hcp structured magnesium phase and a long period stacking ordered structure phase at room temperatures. At least a part of the long period stacking ordered structure phase is flexed or bend.

According to the Embodiment 12, since a casting product is cut into chip-shaped casting products, a fine-grained structure crystal can be obtained. As a result, it becomes possible to produce a plastically worked product having a higher strength, a higher ductility and a higher toughness than that according to the Embodiment 6. In addition, a magnesium alloy according to the embodiment can have a high strength and a high toughness if densities of Zn and rare-earth element are lower than those of the magnesium alloys according to Embodiments 1 to 6.

According to Embodiments 7 to 12, a high strength and high toughness magnesium alloy having a strength and a toughness both being on a level for an alloy to be practically used for expanded applications of a

magnesium alloy, for example, a high technology alloy requiring a high strength and toughness property, and a method of producing the same can be provided.

Example

5 Hereinafter, preferred examples of the present invention will be described.

In Example 1, a ternary alloy containing 97 atomic% of Mg, 1 atomic% of Zn and 2 atomic% of Dy is employed.

10 In Example 2, ternary alloy containing 97 atomic% of Mg, 1 atomic% of Zn and 2 atomic% of Ho is employed.

In Example 3, a ternary alloy containing 97 atomic% of Mg, 1 atomic% of Zn and 2 atomic% of Er is employed.

15 In Example 4, a quaternary alloy containing 96.5 atomic% of Mg, 1 atomic% of Zn, 1 atomic% of Y and 1.5 atomic% of Dy is employed.

In Example 5, a quaternary alloy containing 96.5 atomic% of Mg, 1 atomic% of Zn, 1 atomic% of Y and 1.5 atomic% of Er is employed.

20 Each of the alloys of Examples 4 and 5 is an alloy to which a rare-earth element, which forms a long period stacking ordered structure, is added in combinations.

In Example 6, a quaternary alloy containing 96.5 atomic% of Mg, 1 atomic% of Zn, 1.5 atomic% of Y and 1 atomic% of Dy is employed.

25 In Example 7, a quaternary alloy containing 96.5 atomic% of Mg, 1 atomic% of Zn, 1.5 atomic% of Y and 1 atomic% of Er is employed.

In Comparative example 1, a ternary alloy containing 97 atomic% of Mg, 1 atomic% of Zn and 2 atomic% of La is employed.

5 In Comparative example 2, a ternary alloy containing 97 atomic% of Mg, 1 atomic% of Zn and 2 atomic% of Yb is employed.

In Comparative example 3, a ternary alloy containing 97 atomic% of Mg, 1 atomic% of Zn and 2 atomic% of Ce is employed.

10 In Comparative example 4, a ternary alloy containing 97 atomic% of Mg, 1 atomic% of Zn and 2 atomic% of Pr is employed.

In Comparative example 5, a ternary alloy containing 97 atomic% of Mg, 1 atomic% of Zn and 2 atomic% of Nd is employed.

In Comparative example 6, a ternary alloy containing 97 atomic% of Mg, 1 atomic% of Zn and 2 atomic% of Sm is employed.

20 In Comparative example 7, a ternary alloy containing 97 atomic% of Mg, 1 atomic% of Zn and 2 atomic% of Eu is employed.

In Comparative example 8, a ternary alloy containing 97 atomic% of Mg, 1 atomic% of Zn and 2 atomic% of Tm is employed.

25 In Comparative example 9, a ternary alloy containing 97 atomic% of Mg, 1 atomic% of Zn and 2 atomic% of Lu is employed.

For a reference example, a binary alloy containing 98 atomic% of Mg and 2 atomic% of Y is employed.

(Structure of Casting Material)

First, ingots having compositions according to Examples 1 to 6, Comparative examples 1 to 9 and the reference example were prepared by high frequency melting under an Ar gas environment. Then, a sample 10mm in diameter and 60mm in length was cut out from each of the ingots. And, a structure of each of the casting samples was observed using SEM and XRD. Photographs of the observed structures are shown in Figs.1 to 7.

Fig.1 is photographs showing crystal structures according to Comparative examples 1 and 2.

Fig.2 is photographs showing crystal structures according to Examples 1 to 3.

Fig.3 is a photograph showing a crystal structure according to Example 4.

Fig.4 is photographs showing a crystal structure according to Example 5.

Fig.5 is a photograph showing crystal structures according to Examples 6 and 7.

Fig.6 is photographs showing crystal structures according to Comparative examples 3 to 9.

Fig.7 is a photograph showing a crystal structure according to the reference example.

As shown in Figs.1 to 5, the magnesium alloys according to Examples 1 to 7 have a long period stacking

ordered structure crystal composition formed therein. On the contrary, as shown in Fig.1 and Figs.6 and 7, the magnesium alloys according to Comparative examples 1 to 9 and the reference example do not have a long period 5 stacking ordered structure crystal composition formed therein.

From the observation of Examples 1 to 7 and Comparative examples 1 to 9, the following facts are confirmed.

10 In the Mg-Zn-RE ternary casting alloy, a long period stacking ordered structure is formed therein if RE is Dy, Ho and Er. On the contrary, it is not formed if RE is La, Ce, Pr, Nd, Sm, Eu, Gd and Yb. Gd is slightly different from La, Ce, Pr, Nd, Sm, Eu and Yb in 15 behavior. So, although a long period stacking ordered structure is not formed if Gd is added alone (Zn is necessarily added), when Gd is added together with Y which is an element for forming a long period stacking ordered structure, a long period stacking ordered 20 structure is formed if an addition amount is 2.5 atomic%.

And, when each of Yb, Tb, Sm, Nd and Gd is added to a Mg-Zn-RE (RE=Dy, Ho or Er) alloy at an addition amount of 5.0 atomic% or less, a formation of long period 25 stacking ordered structure is not inhibited. And, when each of La, Ce, Pr, Eu and Mm is added to a Mg-Zn-RE (RE=Dy, Ho or Er) alloy at an addition amount of 5.0

atomic% or less, a formation of a long period stacking ordered structure is not inhibited.

The casting material according to Comparative example 1 has a particle diameter of about 10 to 30 μm , 5 the casting material according to Comparative example 2 has a particle diameter of about 30 to 100 μm and the casting material according to Example 1 has a particle diameter of about 20 to 60 μm . From the observation of these casting materials, a large quantity of 10 crystallization is formed at grain boundaries. And, from the observation of a crystal structure of the casting material according to Comparative example 2, fine precipitation is formed in its particle.

(Vickers Hardness of Casting Material)

15 Each of the casting materials according to Comparative examples 1 and 2 was evaluated in Vickers hardness according to a Vickers hardness test. As a result, the casting material of Comparative example 1 has a Vickers hardness of 75Hv and the casting material 20 of Comparative example 2 has a Vickers hardness of 69Hv.

(ECAE Working)

Each of the casting materials of Comparative Examples 1 and 2 was subjected to an ECAE working at 400°C. The ECAE working was carried out such that the 25 sample was rotated every 90° in the length direction thereof every pass for introducing strain therein uniformly. A number of the pass was 4 times and 8 times.

And, a working rate was constant at 2mm/sec.

(Vickers Hardness of ECAE Worked Material)

Each of the casting material subjected to the ECAE working was evaluated in Vickers hardness according to a 5 Vickers hardness test. The Vickers hardness was measured after 4 times of the ECAE working. As a result, the casting material of Comparative Example 1 has a Vickers hardness of 82Hv and the casting material of Comparative example 2 has a Vickers hardness of 76Hv. So, each of 10 the casting material subjected to the ECAE working is improved in Vickers hardness to about 10% higher than the casting materials before the ECAE working. The casting material subjected to the ECAE working for 8 times has little difference in hardness from the casting 15 material subjected to the ECAE working for 4 times.

(Crystal Structure of ECAE Worked Material)

Composition of each of the casting sample subjected to the ECAE working was observed using SEM and XRD. In the casting materials of Comparative examples 1 and 2, 20 crystallization formed at grain boundaries is decoupled into order of several microns to be dispersed uniformly therein. The casting material subjected to the ECAE working for 8 times shows little difference in structure from the casting material subjected to the ECAE working 25 for 4 times.

(Tensile Strength of ECAE Worked Material)

The ECAE worked casting materials were evaluated in

tensile strength according to a tensile strength test. The tensile strength test was carried out under an initial strain rate of $5 \times 10^{-4}/\text{sec}$ in the parallel direction to a pushing direction. In a case of 4 times 5 of the ECAE working, the casting materials according to Comparative examples 1 and 2 have a yield strength of 200Mpa or lower and an expansion of 2 to 3%.

(Mechanical Property of Extruded Casting Alloys of Examples 8 to 44)

10 Ternary alloys having compositions shown in Tables 1 to 3 were prepared. And, the ternary alloys were heat-treated at 500°C for 10 hours and then extruded at extrusion temperatures and an extrusion rates shown in Tables 1 to 3. The extruded alloys were evaluated in a 15 2% proof stress (a yield strength), a tensile strength and an expansion according to a tensile test at temperatures shown in Tables 1 to 3. The measurements are shown in Tables 1 to 3.

TABLE 1

EXAMPLE	COMPOSITION (at.%)	EXTRUSION TEMPERA- TURE(°C)	EXTRU- SION RATIO	TEMPERA- TURE(°C)	0.2% PROOF STRESS (MPa)	TENSILE STRENGTH (MPa)	EXPAN- SION(%)	HARD- NESS (Hv)
8	Mg-1Zn-0.5Dy	350	10	ROOM TEM- PERATURE	338	340	1	78
9	↓	350	10	200	212	213	10	
10	Mg-1Zn-1Dy	350	10	ROOM TEM- PERATURE	320	321	2.5	85
11	↓	350	10	200	270	275	3	
12	Mg-1Zn-1.5Dy	350	10	ROOM TEM- PERATURE	344	361	6.5	94
13	↓	350	10	200	295	314	6	
14	Mg-1Zn-2Dy	350	10	ROOM TEM- PERATURE	350	385	4	96
15	↓	350	10	200	301	334	5.5	
16	Mg-1Zn-2.5Dy	350	10	ROOM TEM- PERATURE	336	385	7	94
17	↓	350	10	200	314	348	6.5	
18	Mg-1Zn-3Dy	350	10	ROOM TEM- PERATURE	330	387	9	94
19	↓	350	10	200	316	358	6	
20	Mg-0.25Zn-2Dy	350	10	ROOM TEM- PERATURE	310	338	4	83
21	Mg-0.5Zn-2Dy	350	10	ROOM TEM- PERATURE	334	363	4.5	90
22	↓	350	10	200	307	337	7.5	
23	Mg-0.75Zn-2Dy	350	10	ROOM TEM- PERATURE	330	366	4.5	94
24	Mg-1Zn-2Dy	350	10	ROOM TEM- PERATURE	350	385	4	96
25	↓	350	10	200	301	334	5.5	
26	Mg-1.5Zn-2Dy	350	10	ROOM TEM- PERATURE	340	361	8.5	88
27	↓	350	10	200	307	329	10	
28	Mg-2Zn-2Dy	350	10	ROOM TEM- PERATURE	325	347	10	84
29	↓	350	10	200	283	307	13	
30	Mg-2.5Zn-2Dy	350	10	ROOM TEM- PERATURE	280	313	10	80
31	↓	350	10	200	255	276	12.5	

TABLE 2

EXAMPLE	COMPOSITION (at.%)	EXTRUSION TEMPERA- TURE(°C)	EXTRU- SION RATIO	TEMPERA- TURE(°C)	0.2% PROOF STRESS (MPa)	TENSILE STRENGTH (MPa)	EXPAN- SION(%)	HARD- NESS (Hv)
32	Mg-1Zn-2Er	350	10	ROOM TEM- PERATURE	350	385	4	96
33	↓	350	10	200	301	334	5.5	
34	Mg-1Zn-0.5Er	350	10	ROOM TEM- PERATURE	320	330	6	78
35	Mg-1Zn-1Er	350	10	ROOM TEM- PERATURE	270	291	12	80
36	Mg-1Zn-1.5Er	350	10	ROOM TEM- PERATURE	295	321	13.5	88
37	Mg-1Zn-2.5Er	350	10	ROOM TEM- PERATURE	340	375	8	97
38	Mg-1Zn-3Er	350	10	ROOM TEM- PERATURE	300	362	9	98
39	Mg-0.5Zn-2Er	350	10	ROOM TEM- PERATURE	302	327	7	89
40	Mg-1.5Zn-2Er	350	10	ROOM TEM- PERATURE	304	332	10.5	90
41	Mg-2Zn-2Er	350	10	ROOM TEM- PERATURE	284	319	11	84
42	Mg-2.5Zn-2Er	350	10	ROOM TEM- PERATURE	286	311	8	86

TABLE 3

EXAMPLE	COMPOSITION (at.%)	EXTRUSION TEMPERA- TURE(°C)	EXTRU- SION RATIO	TEMPERA- TURE(°C)	0.2% PROOF STRESS (MPa)	TENSILE STRENGTH (MPa)	EXPAN- SION(%)	HARD- NESS (Hv)
43	Mg-1Zn-2Ho	350	10	ROOM TEM- PERATURE	350	385	3	93
44	↓	350	10	200	310	340	8	

These tables shows the measurements of a tensile test and a hardness test at room temperature and at 200°C of casting material having various compositions extruded at a condition of various temperatures, an extrusion rate of 10 and an extrusion speed of 2.5mm/sec.

The present invention is not limited solely to the embodiments specifically exemplified above and various variations may be contained without departing from the scope of the invention.

10 Fig.1 is photographs showing crystal structures of casting materials of Example1, Comparative examples 1 and 2.

Fig.2 is photographs showing crystal structures of casting materials of Examples 2 to 4.

15 Fig.3 is a photograph showing a crystal structure of a casting material of Example 5.

Fig.4 is a photograph showing a crystal structure of a casting material of Example 6.

20 Fig.5 is photographs showing crystal structures of casting materials of Examples 7 and 8.

Fig.6 is photographs shoeing crystal structures of casting materials of Comparative examples 3 to 9.

Fig.7 is a photograph shoeing crystal structures of the reference example.

25 Fig.8 is a view showing a composition range of a magnesium alloy according to the first embodiment of the present invention.

Fig.9 is a view showing a composition range of a magnesium alloy according to the seventh embodiment of the present invention.